CHARACTERIZATION OF VOLATILE SULFUR COMPOUNDS PRODUCED FROM ILLINOIS COAL CHARS

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ABSTRACT

In this study we characterized the major volatile sulfur compounds produced during pyrolysis of chars under different atmospheres and temperatures. To investigate the effects of pyrolysis atmosphere on the evolution of volatile sulfur compounds, an acid-leached char made from high-sulfur Illinois coal was pyrolyzed at 800°C in a hydrogen and in a nitrogen atmosphere. Thiophenic organic compounds were the major products of pyrolysis of the acid-leached char in a hydrogen atmosphere. We then used online pyroprobe-pyrolysis-gas chromatography (PY-GC) to characterize the volatile products evolving at different temperatures from an untreated char, an acid-leached char, and three model chars (a demineralized char and two demineralized chars into which additional sulfur had been incorporated). Hydrogen sulfide gas evolution from the first two chars was measured at progressively increasing temperatures and was found to peak in three temperature regions. Overall, more sulfur gas evolved from the acid-leached char than from the untreated char. Forms of nonmineral sulfur in the char were classified into three types on the basis of the temperatures at which maximum hydrogen sulfide evolution occurred: Type I, elemental sulfur, at 500°C; Type II, weakly-bound sulfur, between 700 and 800°C; and Type III, strongly bound sulfur, at greater than 1000°C.

Study results indicate that elemental sulfur was produced during hydrochloric acid leaching and suggest that the improved rate of sulfur removal observed when char was acid-leached before hydropyrolysis is probably partly due to the conversion of strongly bound mineral sulfur forms to elemental sulfur or weakly bound sulfur forms that can be more easily removed by hydrogen during subsequent hydropyrolysis. The chemical reaction with hydrogen, in addition to heat, was necessary to prevent the elemental sulfur produced during acid leaching and retained in the char from becoming refixed into the char matrix during pyrolysis.

Information provided by this study on the retention of sulfur in char and the reactions involved in its removal may have important implications for the development of coal desulfurization processes using a low-sulfur char made from high-sulfur coal.

INTRODUCTION

As the supply of low-sulfur coal diminishes and interest increases in developing processes that produce low-sulfur char from high-sulfur coal, investigations of the behavior of forms of sulfur in coal during charring and subsequent desulfurization processes are becoming of great significance.

1

Tipton (1977) studied hydropyrolysis desulfurization of a flash pyrolysis char and found that the rate of hydropyrolysis desulfurization could be improved by acid leaching the char before pyrolysis. Kruse and Shimp (1981) studied acid leaching and hydropyrolysis desulfurization of thin-bed char produced from high-sulfur Illinois coal. They leached the char with HCl to produce acid-leached char, which was then hydropyrolyzed at 800°C under a hydrogen atmosphere. They also found that preliminary acid leaching of the untreated thin-bed char was necessary to improve sulfur removal during hydropyrolysis; simple hydropyrolysis alone did not achieve a higher degree of sulfur removal. Acid leaching itself removed only a small percentage of the sulfur, but did remove a large percentage of the iron (Kruse and Shimp, 1981; Shiley et al., 1981). These studies demonstrate the need for a better understanding of how sulfur is retained in coal and char and what types of sulfur reactions are involved in its removal. This study characterizes the major sulfur volatile products evolved during pyrolysis of an acid-leached char and identifies the types of sulfur present in untreated thin-bed char and acid-leached thin-bed char. To explore the relationships among these sulfur forms found in char, we also prepared and analyzed a series of model chars containing different sulfur forms.

EXPERIMENTAL

Preparation of sample chars and model chars

Samples of untreated thin-bed char (TBC) and acid-leached thin-bed char (ALC) were prepared at the Illinois State Geological Survey's Applied Research Laboratory. The thin-bed char was derived from the Herrin (No. 6) Coal Member in Illinois. Elemental analyses of the TBC and ALC are listed in table 1.

Three model chars were prepared. (1) Demineralized char (DMC) was prepared by pyrolysis of demineralized (pyrite removed) low-sulfur coal (C-18824) (Kuhn et al., 1980) at 700°C under nitrogen. (2) Demineralized char containing elemental sulfur (DMC-S_a) was prepared by placing DMC and elemental sulfur (wt ratio 4:1) side by side in a sample tube and then pyrolyzing it under the same conditions used with the other samples, thus allowing elemental sulfur to react with the char upon its volatilization. (3) Demineralized char was also reacted with elemental sulfur (DMC-S_R) by mixing DMC and elemental sulfur (wt ratio 1:1) and then heating the mixture at 480°C for 48 hours under vacuum (Shiley et al., 1981). After cooling, a Soxhlet extraction was performed with methylene chloride for about 2 days to remove any remaining elemental sulfur. Elemental analyses of DMC and DMC-S_R are shown in table 2.

Table 1. Elemental analyses of TBC and ALC.

	TBC (%)	ALC (%)
Carbon	82.78	80.27
Hydrogen	1.67	1.82
Nitrogen	1.50	1.48
Sulfur	2.22	2.00
Chlorine	0.12	2.43

Tube furnace pyrolysis of char: volatile and residue analysis

The char was pyrolyzed in a horizontal tube furnace. Char samples were weighed in porcelain boats and placed inside the opening of the quartz tube, not within the furnace. The inlet end of the tube furnace was then fitted with a push rod and gas inlet tube (Swagelok fittings) to constitute a closed flow system (nitrogen or hydrogen flow gas); the outlet end was fitted with a collection tube immersed in a liquid nitrogen bath. The exiting flow gases were vented in a fume hood. Once set up, the system was purged with flow gas to remove air, and the push rod was used to slide the sample boat into the tube furnace. The temperature of the preheated tube furnace was measured with a calibrated thermocouple set inside the tube furnace. The flow gas swept the volatile products into the collection tube, where they were condensed at liquid nitrogen temperature.

When the collection tube reached room temperature, the gas phase was withdrawn from the headspace with a hypodermic needle and injected directly into a gas chromatograph (GC), and benzene was used to remove the soluble hydrocarbons. Remaining crystals of elemental sulfur (yellow) and ammonium chloride (white) were confirmed by melting point determinations.

Gas phase volatile products were analyzed, using a Perkin-Elmer 3920B GC equipped with a flame photometric detector (FPD). A teflon column (6 ft x 1/8 inches, 5.5-ft packing) packed with acetone-washed PORAPACK QS was used. The injector and detector temperatures were 180°C and 240°C respectively; the column temperature was programmed to hold at 80°C for 1 minute, then increase at a rate of 8°C/min to a final temperature of 200°C, where it was held for 1 minute. The flow rate of carrier gas (helium) was 18 mL/min.

Solvent extract analysis was accomplished by coupling the GC with an Envirochem Unicon 810A concentrator. A methyl silicone-fused silica capillary column (24 m x 0.20 mm, Carbowax x 20 m deactivated) was used and the column temperature was programmed to hold at 40°C for 2 minutes, then increase at a rate of 4°C/min to a final temperature of 260°C, where it was held for 8 minutes. Liquid and gaseous volatiles were identified by coinjection of standards. Some of the identifications were verified by GC-mass spectrometric analysis.

Pyrolysis residues were cooled in an inert atmosphere and collected for weight measurement and elemental analysis. Elemental analysis was performed with a CARLA-ERBA C, H, and N analyzer.

Table 2. Elemental analyses of DMC and DMC1-S_R

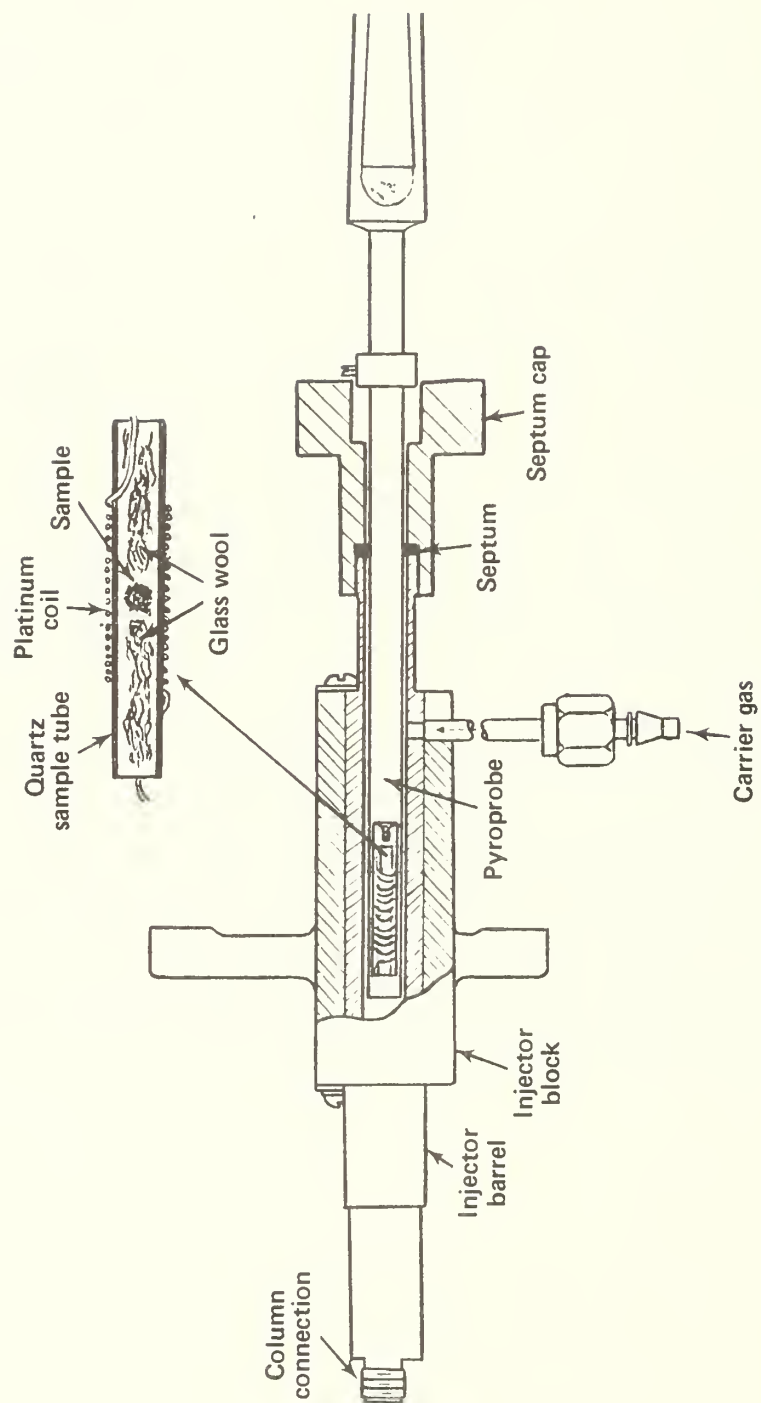|	DMC (%)	DMC1-S_R (%)
Carbon	86.24	74.77
Hydrogen	1.61	0.57
Nitrogen	1.98	1.63
Sulfur	0.01	20.42

Figure 1 A Chemical Data System pyroprobe 190 incorporated on-line pyrolysis gas chromatography volatile analysis injector system.

4

Pyroprobe-pyrolysis-GC/FPD characterization of chars

TBC and ALC samples were pyrolyzed in stages at progressively higher temperatures under helium atmosphere, and the gaseous volatile materials were analyzed by GC. A Chemical Data Systems Pyroprobe 190 was incorporated directly into the GC injector (fig. 1) to permit pyrolysis and subsequent characterization of the volatile products. The char sample was placed inside a quartz tube that was inserted into the heating coil at the end of the pyroprobe. The pyroprobe was then inserted into the GC injector. Each sample was pyrolyzed at seven consecutively increasing temperatures (400, 500, 600, 700, 800, 900 and 1000°C). The temperature was increased at a rate greater than 800° C/sec (ramp rate setting on "off" position) and held at each temperature for 20 seconds. GC analysis of the products produced at each temperature was conducted under the same conditons used for volatile gas analysis during ALC pyrolysis. Seven GC chromatograms were produced for each sample and the GC response of each sulfur-containing gas was measured on each chromatogram. A plot of GC response versus pyrolysis temperature was made for each sample.

RESULTS AND DISCUSSION

Tube furnace pyrolysis of char: volatile analysis

ALC was pyrolyzed either at 800°C in a hydrogen atmosphere (H_2-pyrolysis) or at 800°C in a nitrogen atmosphere (N_2-pyrolysis). The volatiles were condensed in a collection tube under liquid nitrogen. The products were then separated and analyzed.

The four major sulfur gases produced during N_2-pyrolysis of ALC were hydrogen sulfide (H_2S), carbonyl sulfide (COS), sulfur dioxide (SO_2), and carbon disulfide (CS_2). H_2S was the major sulfur gas (>98%) volatilized during H_2-pyrolysis. Under both pyrolysis conditions volatiles that solidified were produced—ammonium chloride (NH_4Cl) and elemental sulfur (S_8).

The GC traces of benzene-extractable volatiles produced during H_2-pyrolysis and N_2-pyrolysis are shown in figures 2 and 3. Hydrocarbons were detected by an FID detector and sulfur compounds by an FPD detector.

The GC-FID chromatograms of the hydrocarbon volatiles produced under H_2-pyrolysis and N_2-pyrolysis of ALC are shown in figure 4. The GC-FPD chromatograms of the sulfur-containing compounds produced under H_2-pyrolysis and N_2-pyrolysis are shown in figure 5. The sulfur compounds produced during H_2-pyrolysis consist mostly of thiophenic organic sulfur compounds (thiophene, benzothiophene, and dibenzothiophene). A comparison of the GC traces of H_2-pyrolysis and N_2-pyrolysis, shows that thiophenic organic sulfur compounds did not volatilize during pyrolysis under nitrogen; this suggests that the production of thiophenic organic sulfur compounds did not occur as a consequence of heat alone, but as a result of direct reaction with hydrogen gas during pyrolysis.

Tube furnace pyrolysis of char: residual analysis

The first step in consecutive pyrolyses of acid-leached char (ALC) was to pyrolyze the ALC at 300°C under a nitrogen flow. The residual char (ALC1) was pyrolyzed at 800°C under nitrogen to produce ALC2, which was then pyrolyzed at 800°C under hydrogen to form residue char ALC3. Another sample of ALC was pyrolyzed at 800°C under a hydrogen gas flow to produce ALC4.
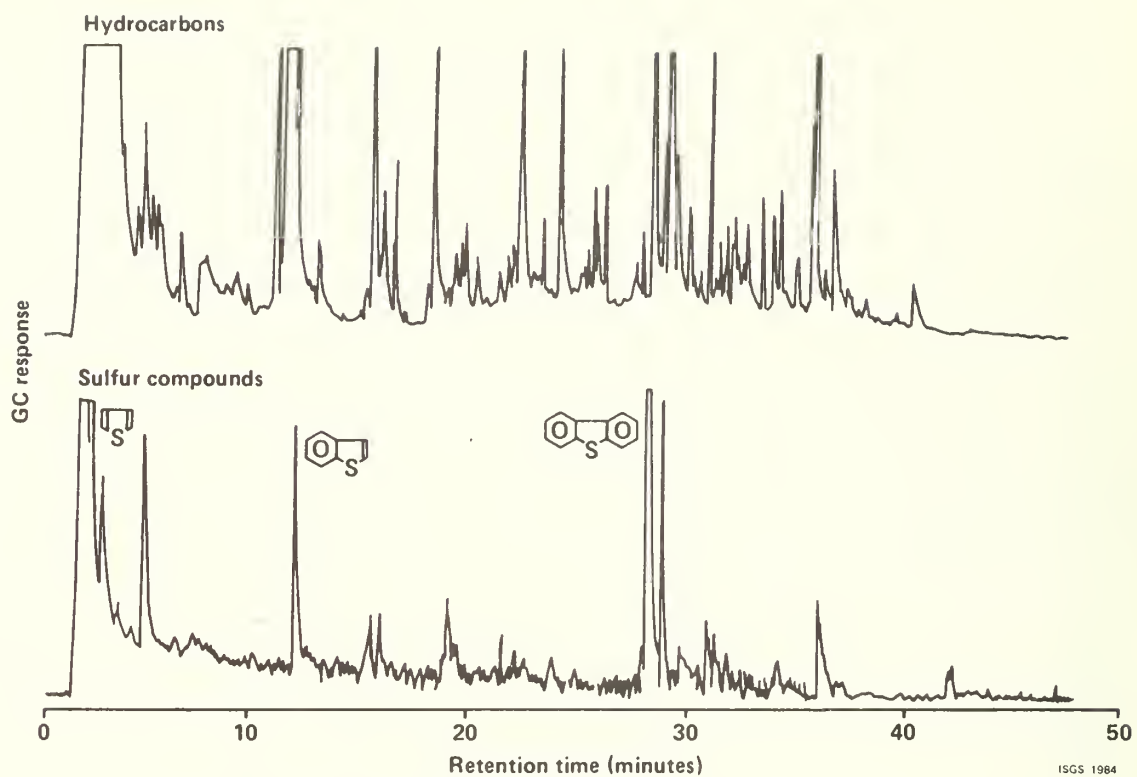
Figure 2 Typical GC traces of benzene extractable volatiles produced during H_2-pyrolysis of ALC.
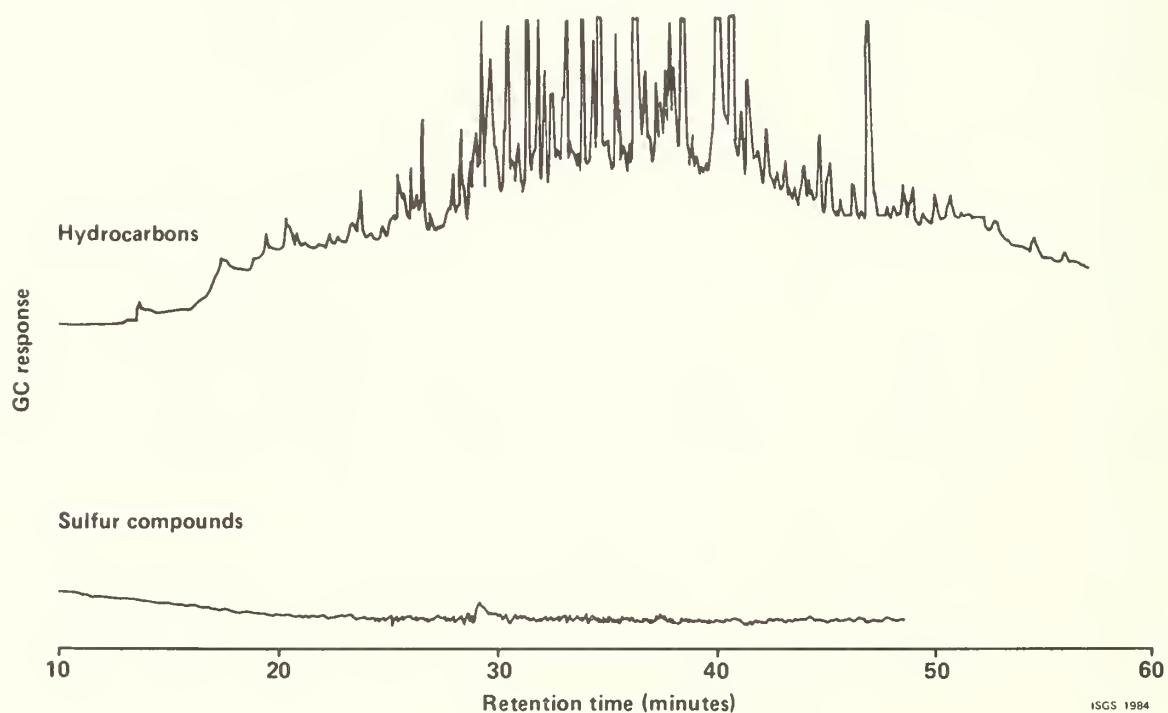

Figure 3 Typical GC traces of benzene extractable volatiles produced during N_2-pyrolysis of ALC.
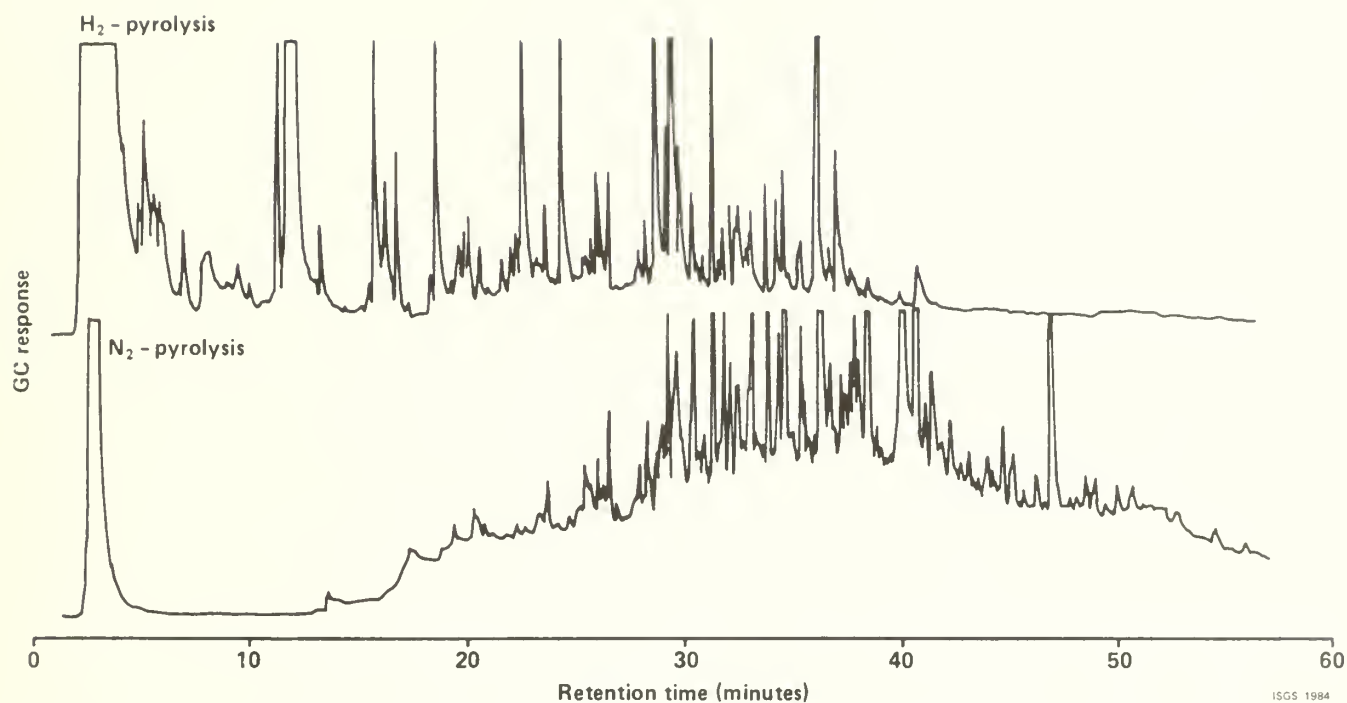
Figure 4 GC-FID traces of hydrocarbons volatilized during pyrolysis of ALC under hydrogen (H₂-pyrolysis) and under nitrogen (N₂-pyrolysis).
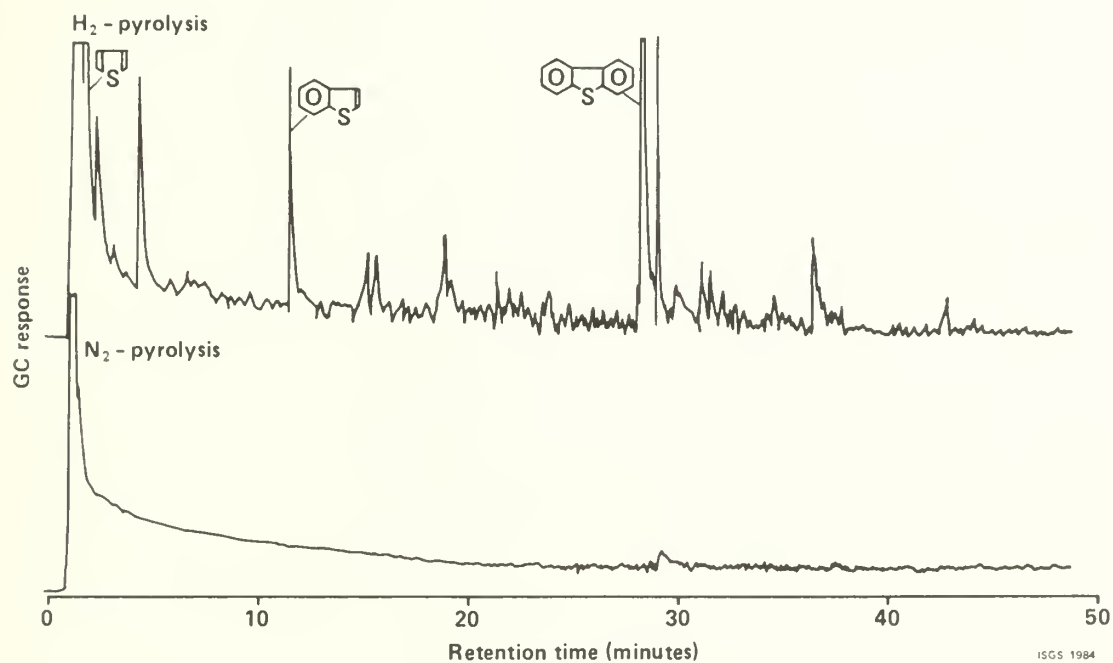

Figure 5 GC-FPD traces of sulfur compounds volatilized during pyrolysis of acid-leached char under hydrogen (H₂-pyrolysis) and under nitrogen (N₂-pyrolysis).

Table 3. Elemental analysis of acid-leached char and a series of residue chars produced from pyrolysis of ALC.

Sample ID	Sample				
% (moisture free)	ALC	ALC1	ALC2	ALC3	ALC4
Hydrogen	1.82	1.70	0.69	0.61	0.68
Carbon	80.27	82.38	82.38	90.40	91.63
Nitrogen	1.48	1.50	1.53	1.30	1.00
Sulfur	2.00	2.03	1.97	0.42	0.26
Chlorine	2.43	1.31	0.03	0.02	0.02

Results of elemental analysis of the ALC, ALC1, ALC2, ALC3, and ALC4 are shown in table 3. The weight loss and sulfur loss determined after each stage of pyrolysis are shown in figure 6. Weight losses (based on 100 g of ALC) during each stage were 6.41 g at 300°C, N_2 atmosphere; 8.59 g at 800°C, N_2 atmosphere; and 1.35 g at 800°C, H_2 atmosphere. ALC contained 2.00 g sulfur per 100 g. The corresponding sulfur losses during pyrolysis were 0.12 g, 0.22 g, and 1.32 g respectively. We observed that the maximum sulfur loss occurred at 800°C during the H_2 step and that no large weight loss occurred in this stage of pyrolysis. This result strongly suggests that chemical reaction with hydrogen was responsible for the major removal of sulfur during hydropyrolysis of the acid-leached char. Hydrogenation is necessary to prevent the sulfur compounds being liberated by heat and the elemental sulfur produced and retained during acid-leaching from being refixed into the char matrix by a secondary reaction during pyrolysis.

Pyroprobe-pyrolysis GC analysis of chars and model chars
The major sulfur gases obtained during pyroprobe pyrolysis of coal chars were identified, on the basis of GC retention time and mass fragmentation data, as H_2S, COS, SO_2, and CS_2. Typical GC-FPD traces of these gases are shown in figure 7.

The evolution of sulfur-containing gases versus pyrolysis temperature of both ALC and TBC was plotted in figures 8 and 9. The GC response is a relative measure of the quantity of gas produced at a given pyrolysis temperature. The GC response of the gas versus overall pyrolysis tempera-
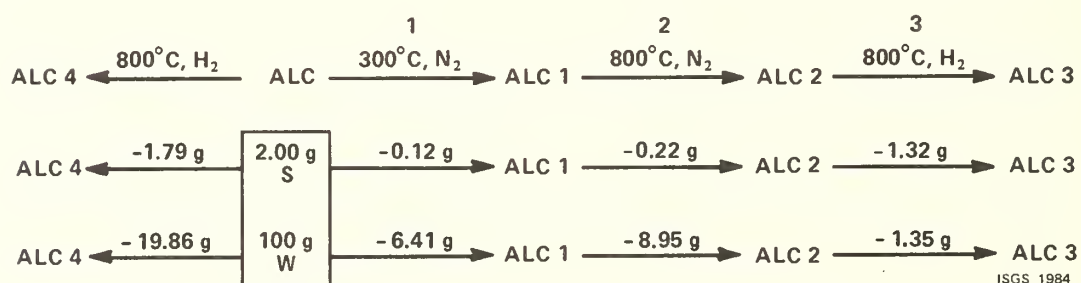

Figure 6 Weight loss and sulfur loss after each stage of pyrolysis of ALC.

8

ture is referred to as a pyrogram. A comparison of the two pyrograms shows that more sulfur gas is produced from ALC than from TBC. However, similar trends in H_2S, COS, SO_2, and CS_2 production are found in both pyrograms.

To examine this further, we plotted the H_2S production curves for ALC and TBC on the same set of coordinate axes in figure 10.

These GC response curves illustrate that sulfur gas production from ALC was greater than sulfur gas production from TBC. Three regions of maximum H_2S evolution occurred in both curves: region I occurs at a pyrolysis temperature of approximately 500°C, region II at a pyrolysis temperature of between 700° and 800°C, and region III at a pyrolysis temperature greater than 1000°C. The three regions of maximum H_2S evolution appear to be related to different types of sulfur-containing species characterized by different sulfur bonding energies. To investigate this hypothesis, we studied model chars containing different sulfur forms.
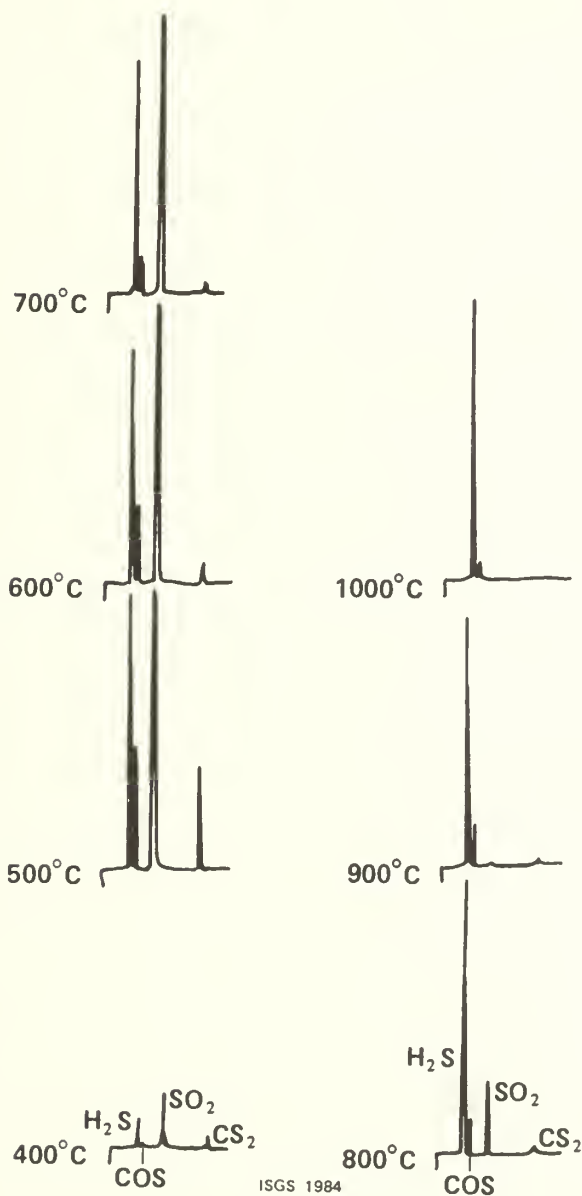

Figure 7 GC traces of the major sulfur gases evolved from ALC at consecutive pyrolysis temperatures.
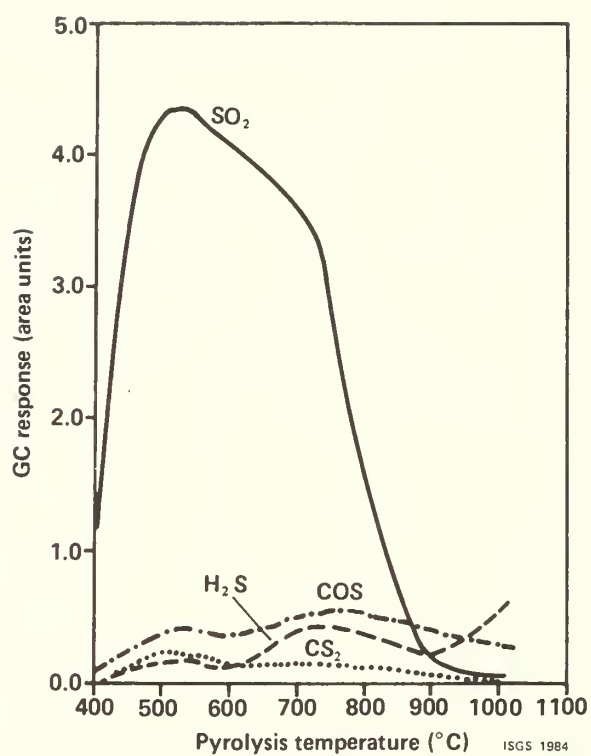
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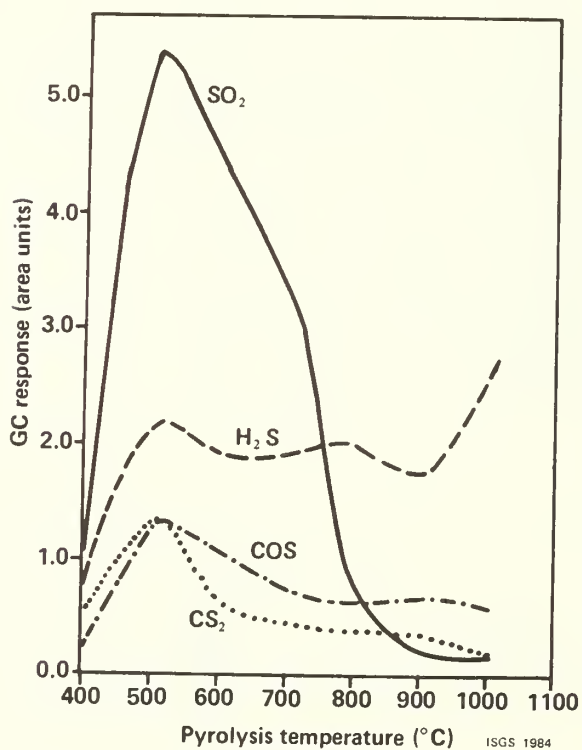
Figure 8 Sulfur gas pyrogram for TBC.

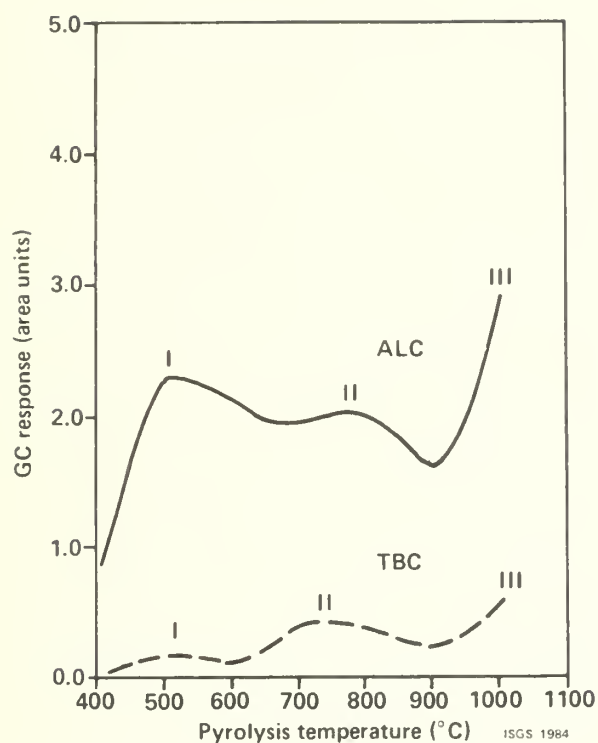**Figure 9** Sulfur gas pyrogram for ALC.

Figure 10 Hydrogen sulfide (H$_2$S) evolution of TBC and ALC during pyrolysis.

Each model char was analyzed by the stepwise pyrolysis GC-FPD method. The pyrograms of these model chars (figs. 11, 12, and 13) are different, which suggests the presence of different types of sulfur that can be volatilized as sulfur gases. A plot of H$_2$S response versus pyrolysis temperature for each model char is shown in figure 14. The H$_2$S pyrogram for each model char has a region of maximum H$_2$S evolution corresponding to one of the three regions of maximum H$_2$S evolution for ALC and TBC. This suggests that the sulfur present in each model char is similar to one of the sulfur forms present in TBC and ALC. DMC (low-sulfur demineralized char) has a point of maximum H$_2$S evolution above 1000°C, which corresponds to region III of the H$_2$S curves of ALC and TBC. Because high heating temperatures ($>$900°C) were required to liberate the sulfur remaining in demineralized char, this sulfur is thought to be relatively strongly bound. The H$_2$S pyrogram for DMC-S$_a$ (DMC with elemental sulfur adjacent) shows a maximum point of H$_2$S evolution at about 500°C, which corresponds to region I of the H$_2$S curves of the chars. This indicates that some of the sulfur in TBC and ALC is elemental sulfur. A separate part of this study showed that more than 15 percent of the sulfur in ALC can be removed by cyclohexane extractions. The H$_2$S pyrogram for DMC-S$_R$ (methylene chloride extracted) has maximum H$_2$S evolution at about 780°C; this corresponds to region II of the H$_2$S curves, and may be indicative of a weakly bound sulfur species.

Results of a study of the dehydrogenation of coal by reaction with elemental sulfur (Mazumadar et al., 1982) suggest that part of the sulfur remaining in coals appears to be chemically combined and that possibly R-S-R type and/or R-S-S-R type linkages are brought about in the reaction.
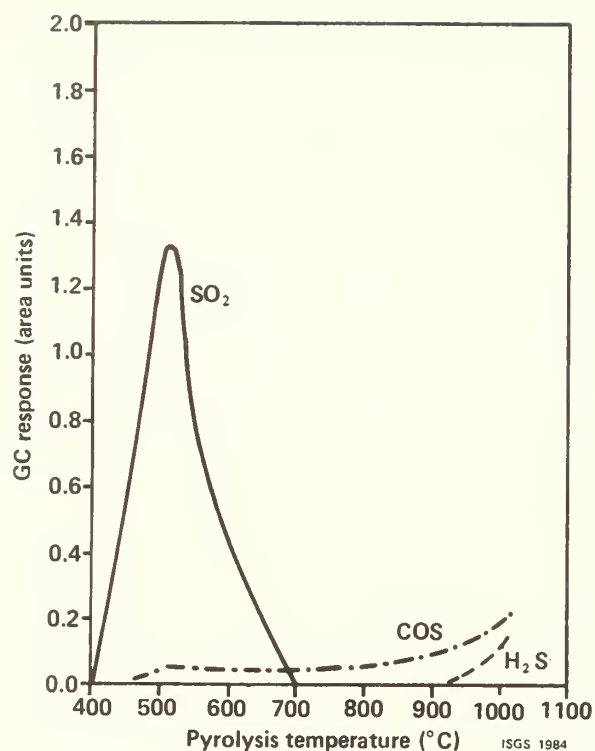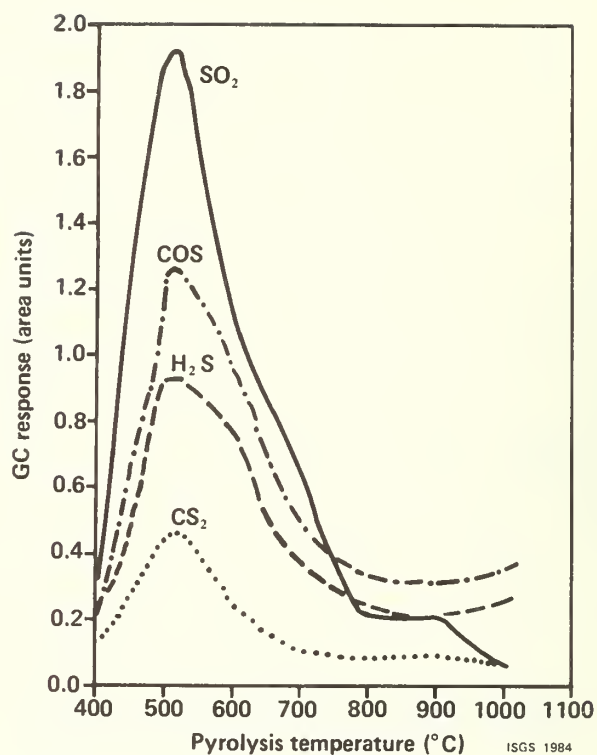
Figure 11   Sulfur gas pyrogram for DMC.
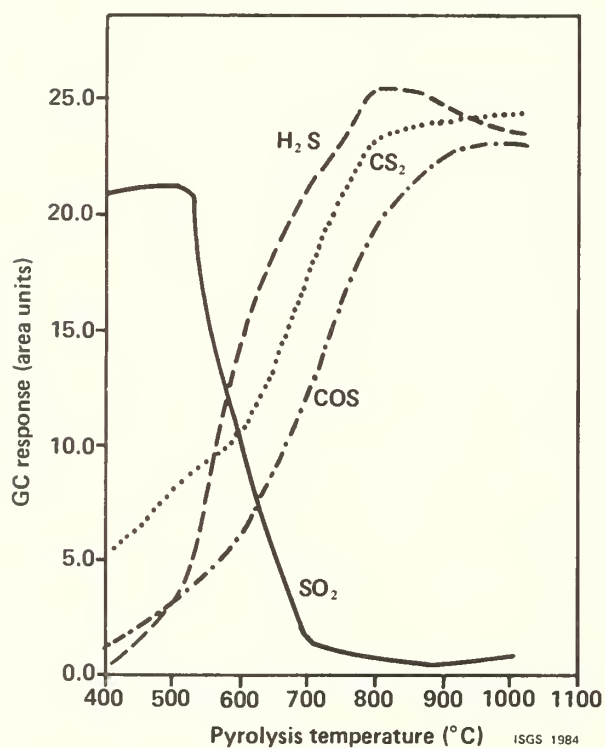

Figure 12   Sulfur gas pyrogram for DMC-S_a.

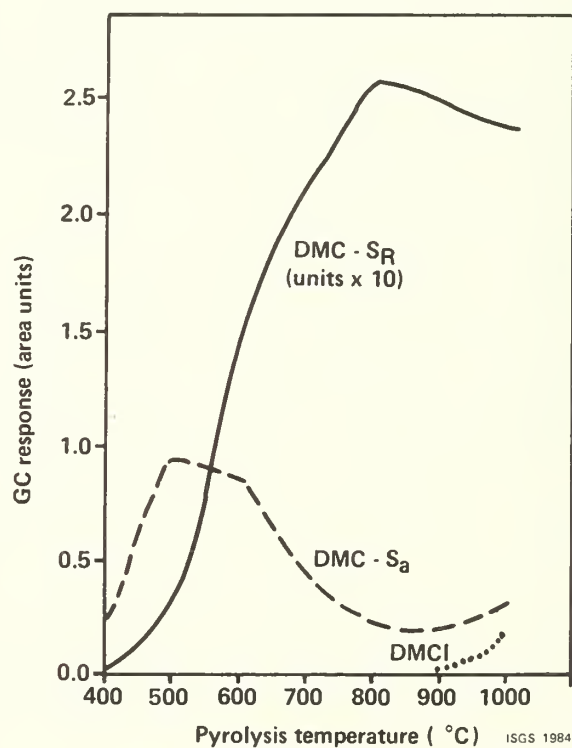**Figure 13**   Sulfur gas pyrogram for DMC-S_R.

Figure 14 H_2S evolution of model chars during pyrolysis.

A study by Kamishita (1976) suggests that freshly prepared chars can chemisorb oxygen on exposure to air at room temperature. Although there is a possibility that sulfur may be physically trapped in the char matrix, we suggest, on the basis of these two studies and our own study, that a chemisorption for type II and type III sulfur occurs in the char.

During acid leaching of the char an increase occurred in the production of all three types of sulfur (fig. 10). (Type I sulfur was more abundant than type II sulfur.) A Mossbauer study of TBC and ALC (Shiley et al., 1981) revealed that iron sulfides were the major compounds dissolved by acid leaching. This suggests that the production of types I, II, and III sulfur is a consequence of the release of iron-bound sulfur during acid leaching; it also suggests that the improvement of the hydrodesulfurization rate in chars that have undergone acid leaching is due partly to the conversion of strongly bound mineral sulfur, which resists hydrogen attack under the pyrolysis conditions (Cypre, Ghodsi, and Stock, 1981; Gallo, 1927), to elemental sulfur or more weakly bound sulfur which are more easily removed by hydrogen.

CONCLUSIONS

In this study we classified forms of nonmineral sulfur in char into three types based on the temperature at which hydrogen sulfide evolution occurred during pyrolysis:

Type I: Elemental sulfur, characterized by maximum evolution of H_2S at $500°C$.

Type II: Weakly bound sulfur, characterized by maximum evolution of H_2S between 700 and $800°C$.

Type III: Strongly bound sulfur, characterized by maximum evolution of H_2S at temperatures greater than $1000°C$.

The improvement of hydrodesulfurization in char after acid leaching is probably due in part to the conversion of strongly bound mineral sulfur, which resists hydrogen attack under the pyrolysis conditions, to elemental sulfur or weakly bound sulfur forms that are more easily removed by hydrogen.

Heat alone did not remove sulfur efficiently from the acid-leached char; a chemical reaction with hydrogen, in addition to heat, was necessary to prevent the elemental sulfur produced and retained in acid-leached char from becoming refixed into the char matrix during pyrolysis of the char in an inert atmosphere.

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